# United States Patent [19]

**Watarai et al.**

[11] **3,874,943**

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[54] **SENSITIZERS FOR ELECTROPHOTOGRAPHY**

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[51] **Int. Cl.** ............................................... **G03g 5/04**

[58] **Field of Search** ............................ 96/1.5, 1.6, 1

[56] **References Cited**

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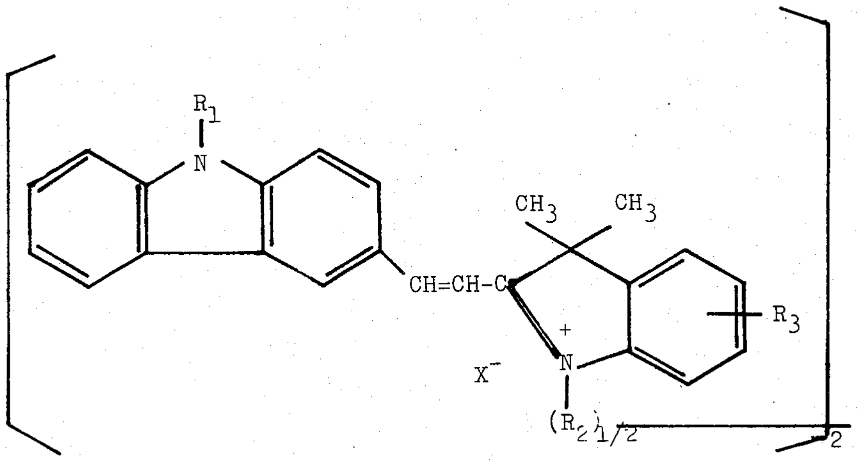
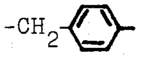
[57] **ABSTRACT**

A novel sensitizer effectively sensitizing an organic photoconductor for electrophotography comprising the dimerized cyanine dye having a carbazole nucleus represented by the following general formula



wherein $R_1$ represents a hydrogen atom; an alkyl group having 1–5 carbon atoms; an alkyl group substituted by a halogen atom, a hydroxyl group or a cyano group; or an acyl group substituted by a halogen atom, a hydroxyl group, or a cyano group; $R_2$ represents —$(CH_2)_n$ (where *n* is a positive integer of 2 to 6) or



$CH_2$—; $R_3$ represents a hydrogen atom, a halogen atom, a nitro group, an alkyl group having 1–5 carbon atoms, —OR′, or —COOR′ (where R′ is an alkyl group having 1–5 carbon atoms); and X represents an anion residue.

**6 Claims, No Drawings**

# SENSITIZERS FOR ELECTROPHOTOGRAPHY

## BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a sensitizer for an electrophotograhic photosensitive material comprising an organic compound as the photoconductor.

2. Description of the Prior Art

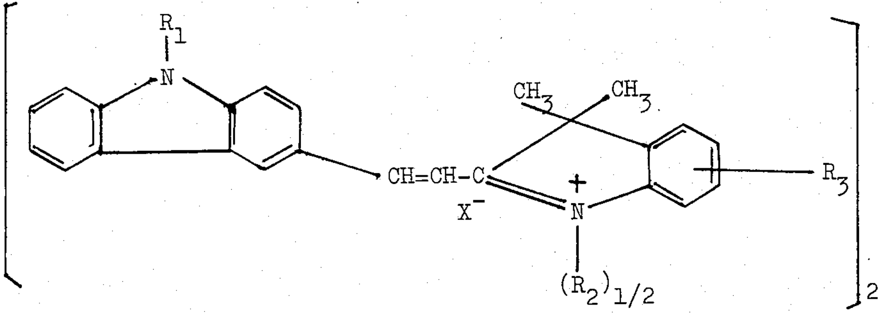
In electrophotograhic techniques using an organic photoconductor, the most important factor affecting the sensitivity thereof is the sensitizer used.

Hitherto, polyvinyl heterocylic compounds typified by poly-n-vinylcarbazole, polynuclear aromatic vinyl polymers such as polyvinyl anthracene; and other low molecular weight compounds having a heterocyclic ring such as an oxazole nucleus, a thiazole nucleus, and the like have been used as photoconductors for electophotography, but they themselves have sufficient sensitivity.

## SUMMARY OF THE INVENTION

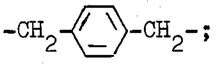
The present invention has as its object the provision of a novel sensitizer capable of improving the sensitivity and the sensitive wave length region of such organic photoconductors by additon thereto.

The sensitizer of this invention is a dimerized cyanine dye having a carbazole nucleus represented by the following general formula I:



I

wherein $R_1$ represents a hydrogen atom; alkyl group having 1–5 carbon atoms; an alkyl group substituted by a halogen atom, a hydroxyl group, or a cyano group; or an acyl group substituted by a halogen atom, a hydroxyl group, or a cyano group; $R_2$ represents $-(CH_2)_n-$ (*n* is a positive integer of 2 to 6) or



$R_3$ represents a hydrogen atom, a halogen atom, a nitro group, an alkyl group having 1–5 carbon atoms, —OR', or —COOR' (where R' is an alkyl group having 1–5 carbon atoms); representative of these alkyl groups being methyl, ethyl, propyl butyl or pentyl groups; representatives of the halogen atoms being a chrorine, bromine or iodine atom; and representative of the acyl groups, are those of the formula $R_4CO$— (wherein $R_4$ is an alkyl group having 1 to 3 carbon atom, benzyl or toluyl group); and X represents an anion residue, i.e., an anion residue capable of forming a cyanine salt as is generally used in the cyanine dye art. $X^-$ can be organic or inorganic. Typical representatives of $X^-$ are halogen atoms such as Cl, Br, I, materials such as $BF_4$, $ClO_4$,

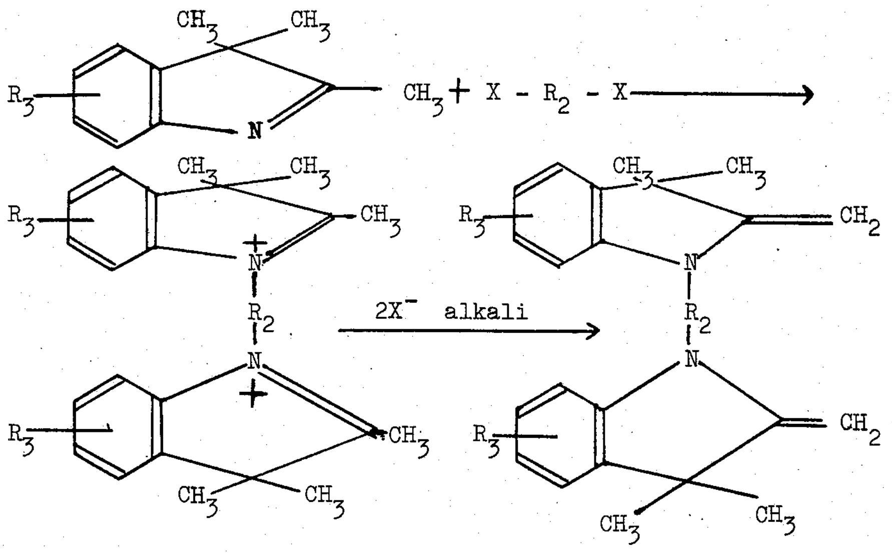
and the like. X is not limited to the above materials and can be freely selected.

In the above formula, for example, when a dimer is represented as $A—R_2—A$, one part thereof can be shown as $(A—R'_2)_2$, where $R_2=R_2'—R_2'$. In such a case, the abbreviation of $R_2'—R_2'$ is given as $(R_2)_{1/2}$.

## DETAILED DESCRIPTION OF THE INVENTION

Many dyes having one cyanine structure in one molecule have been synthesized and used, but a dye having two cyanine structures in one molecule has not been known. The inventors succeeded in synthesizing a dye having two cyanine structures in one molecule by dimerizing an indoline derivative which is the nucleus forming a cyanine dye.

More practically speaking, a method of synthesizing a dimer indoline through the N-position of an indoline derivative is profitably used, that is to say, the following reaction is used:



wherein $R_2$, $R_3$, and X have the same significance as in general formula I, $R_2$ being a bonding group having the action of forming the dimer by bonding the nitrogen atom.

The 2,3,3-trimethylindolenine derivative used as a raw material in the above reaction are know and largely produced as intermidates for cyanine dyes and other dyes. The alkyl dihalide and xylylene halide ($X—R_2—X$) used in the above reaction is readily available.

The synthsis of the dimer of 2-methylene indoline will now be further explaned in detail. When the 2,3,3-trimethylindolenine having the substituents as shown in the following Compound group I is quaternarized by the alkyl or xylylene halide as shown in compound group II shown below to form a dimerized quaternary salt through the alkyl group at the N-position and then the quaternary salt is neutralized with an alkali or a base, a 2-methyleneindoline dimer is obtained.

For example, two mols of a compound of group I can be reacted with one mol of an alkyl dihalide at a temperature of from about 80° to 150°C at normal pressure for about 2 to 15 hours. The neutralization then is performed with an alkali material, most commonly sodium hydroxide.

Regarding the neutralization, since the dimerized quaternary salt is insoluble in water, it is dissolved by heating to about 80°C and after the dissolution the alkali (basic) material is added to raise the pH to greater than 7. The exact conditions of neutralization merely follow neutralization conditions for similar materials known in the prior art.

In the reaction of the present invention, a solvent can be used if desired, but it is not necessary. When a solvent is used, excellent results are obtained when the solvent is from about one half to five times the weight of the reactants.

## COMPOUND GROUP I

Compound No. 1: 2,3,3trimethylindolenine,
Compound No. 2: 5-methyl-2,3,3-trimethylindolenine,
Compound No. 3: 5-ethyl-2,3,3-trimethylindolenine,
Compound No. 4: 5-propyl-2,3,3-trimethylindolenine,
Compound No. 5: 5-butyl-2,3,3-trimethylindolenine,
Compound No. 6: 5-pentyl-2,3,3-trimethylindolenine,
Compound No. 7: 5-chloro-2,3,3-trimethylindolenine,
Compound No. 8: 5-bromo-2,3,3-trimethylindolenine,
Compound No. 9: 5-nitro-2,3,3-trimethylindolenine,
Compound No. 10: 5-methoxy-2,3,3-trimethylindolenine,
Compound No. 11: 5-ethoxy-2,3,3-trimethylindolenine,
Compound No. 12: 5-propoxy-2,3,3-trimethylindolenine,
Compound No. 13: 5-carbomethoxy-2,3,3-trimethylindolenine,
Compound No. 14: 5-carboethoxy-2,3,3-trimethylindolenine.

## COMPOUND GROUP II:

Compound No. 15: 1,2-dibromoethane,
Compound No. 16: 1,2-dichloroethane,
Compound No. 17: 1,3-dibromopropane,
Compound No. 18: 1,4-dibromobutane,
Compound No. 19: 1,5-dibromopentane,
Compound No. 20: 1,6-dibromohexane,
Compound No. 21: xylylene chloride.

In a specific example of the synthesis of a dimer cyanine dye, when 25.6 g of compound No. 1 (2,3,3-trimethylindolenine) and 17.2 g of 1,4-dibromobutane are heated at 130°C for 3 hours, the whole reaction mixture solidifies. The crystals formed are collected in acetone, dissolved in water, and the aqueous solution is neutralized by adding aqueous sodium hydroxide solution, whereby a solid material is deposited. When the solid material is collected and recrystallized from ethanol, 6.8 g of crystals melting at 103°C are obtained.

The crystals have an absorption at 1635 $cm^{-1}$ based on an exo-methylene group (shown by infrared absorption spectra).

Elementary analysis: H,8.61; C,84.15; N,7.52. (calculated: H,8.66; C,83.82; N 7.52).

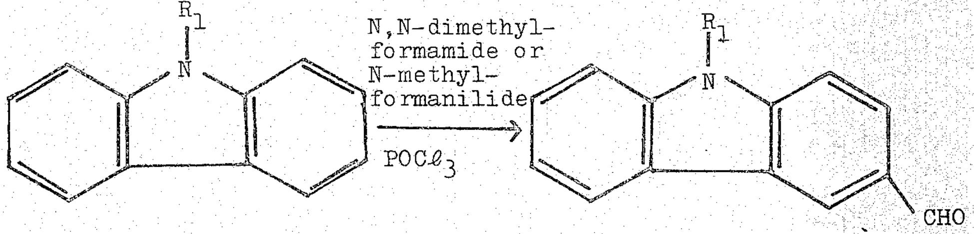
From the above analytical data, it was confirmed that N,N'-butylenebis-(3,3-dimethyl-2-methyleneindoline) was obtained.

N,N'-xylylenebis-(3,3-dimethyl-2-methyleneindoline) is prepared, in another example, by heating compound No. 1, (2,3,3-trimethylindolenine) and compound No. 21, (xylylene chloride) in toluene to quaternarize the former. The quaternary salt is neutralized with alkali. The compound has a melting point of 137°C.

By a similar procedure, that is, merely by alternating the starting materials, various derivatives of 2-methyleneindoline dimers can be synthesized by reacting various combinations of the compounds belonging to compound group I and compounds belonging to compound group II.

To prepare a cyanine dye having a carbazole nucleus using the 2-methyleneindoline dimer thus synthesized, a formyl group can be introduced into the carbazole to condense the cyanine dye. The introduction of the formyl group into the carbozole derivative can be conducted utilizing a Vilsmeier reaction as described in the report of N. G. Ph. Buu-Hoi & N. G. Hoan, "Carbazole Aldehydes" in "The Journal of the American Chemical Society", 73, 98(1951), published by The American Chemical Society, Washington D.C.

This reaction is shown by the following formula:



The preparation of the formylated carbazole is illustrated in further detail by the following experiments. Needless to say, it is also possible to introduce such a formyl group based on the description in the Buu-Hoi article heretofore given utilizing the Vilsmeier reaction as described therein.

The formylation is preferably conducted at a pressure of 1 atm. pressure, a temperature of 40°–100°C and over a time of 1–10 hours. 1 to 3 mols of $POCl_4$ is preferred to 1 mol of carbazole, in combination with 1.5–20 mols of DMF being preferred to 1 mol of carbazole. A solvent is not necessary when DMF is used, but a solvent is used when N-MFA is used, for example as described in Experiment 1 below.

## EXPERIMENT 1

The case of $R_1 = CH_3$: A mixture of 65 g of 9-methylcarbazole, 64 g of N-methylformanilide, 64 g of phosphorus oxychloride, and 50 ml of o-dichlorobenzene was heated on boiling water bath at normal pressure for 6 hours. After cooling, the reaction product was treated with a 30% aqueous sodium acetate solution and then subjected to steam distillation to remove o-dichlorobenzene (solvent) and N-methylaniline. The residue was extracted with benzene and the benzene extract was concentrated and distilled to give 9-methyl-3-formylcarbazole having a melting point of 74°C.

## EXPERIMENT 2

The case of $R_1 = C_2H_5$: 127 g of phosphorus oxychloride was placed in a three-necked flask and 100 ml of N,N-dimethylformamide was added dropwise thereto at 10°–15°C with stirring. A solution of 122 g of N-ethylcarbazole in 100 ml of N,N-dimethylformamide was added dropwise to the mixture at room temperature. Then, after stirring the resultant mixture while heating for 5 hours at 50°C, the mixture was allowed to stand overnight. When the reaction product was poured into a large amount of water and the solution was neutralized with an aqueous $NaHCO_3$ solution, a yellow-white precipitate was formed. By recrystallizing the precipitate from ethyl alcohol, 9-ethyl-3-formylcarbazole having a melting point of 89°C. was obtained. All of the above procedures were performed at normal pressure.

In a similar manner other formylated carbazoles can be produced, i.e., merely by alternating the starting materials, one can use the same reaction conditions to obtain other formylated carbazoles.

The dye having two cyanine structures in one molecule which is the dye used in this invention, can be produced by any one of the following two methods:

i. The dye is prepared by heating the dimer (bisindolenium salt) quaternarized by the reaction of an indolenine and the alkyl dihalide as described above together with formylated carbazole in a dehydrated solvent such as acetic anhydride. In this reaction, usually 1 mol of dimer to 2 mols of carbazole permits reaction to proceed at an excellent pace. The reaction proceeds easily under normal pressure, and preferred temperatures of operation of from about 60° to about 80°C. From about 1 to about 6 hours at such temperatures insures reaction completion. Though not overly important, a solvent can be used in an amount of about 5 to 20% by weight, based on the total weight of reactants. Additional examples of the solvents used in this reaction are N,N-dimethyl formamide, dimethyl sulfoxide and hexmethylphosphoamide.

ii. The dye is prepared by treating the bisindolenium salt with an alkali to form a 2-methyleneindoline dimer and the dimer then reacted in the presence of formylcarbazole and an acid. In this process, commonly used alkali materials are sodium and potassium hydroxide, and the alkali should be used in a molar excess with respect to the bisindolenium salt. 1 mol of the dimer to 2 mols of the carbazole permits the reaction to proceed smoothly, especially when more than 2 mols of acid is present per mol of dimer. The reaction proceeds smoothly at normal pressure and at a temperature of from about 50°C to the boiling point of the solvent used, with about 1 to about 6 hours insuring complete reaction. Typical of the acids used are hydrogen halide, such as hydrogen chloride, hydrochloric acid, hydrogen bromide, boron fluoride, perchloric acid, p-toluene sulfonic acid and the like. If a solvent is used for the reaction, it is preferred to use such in an amount similar to that described for reaction I) above. Useful solvents include cyclic ethers such as tetrahydrofran diorxanes, alcohols having from 1 to 4 carbon atoms such as methanol, ethanol propanol, butanols; aromatic hydrocarbons such as benzene, toluene, etc.

Specific examples of method (ii) described above are shown below.

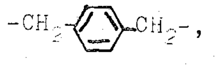
## SYNTHESIS I

3.72 g of N,N'-butylenebis(3,3-dimethyl-2-methyleneindoline) and 4.5 g of N-ethyl-3-formylcarbazole were dissolved in 100 ml of ethyl alcohol, and after adding to the solution three drops of piperidine, the mixture was refluxed at the boiling point of ethyl alcohol for 4 hours. When hydrogen chloride gas was passed through the solution, the solution colored red-purple and then the dye formed precipitated. Hydrogen chloride gas was passed through the solution in an amount slightly more than the equilmolar amount relative to the carbazole at 30°–50°C. After passing sufficient hydrogen chloride therethrough, the solution was allowed to stand overnight. Since it was difficult to obtain the product in the form of the hydrochloride, the reaction product was poured into an aqueous 10% by weight perchloric acid solution in slight excess over the carbazole (generally in an amount of 1–1.2 mol to the carbazole) and then recovered as the perchlorate to give 1.2 g of the dye.

The absorption maximum wave length of the product was at 533 mμ in chloroform. The compound thus produced corresponds to the compound of general formula I wherein $R_1$ is an ethyl group, $R_2$ is $-(CH_2)_4-$, $R_3$ is H, and X is $ClO_4$.

## SYNTHESIS II

In the same way as in Synthesis I, the dye corresponding to the compound of general formula I wherein $R_1$ is an ethyl group, $R_2$ is



$R_3$ is H and X is $ClO_4$ was produced from N,N'-xylylenebis(3,3-dimethyl-2-methyleneindoline) and

N-ethyl-3-formylcarbazole. The absorption maximum wave length of the dye was at 544 m$\mu$ in chloroform.

It will understood that in a similar manner cyanine dye having various substituents as $R_1$, $R_2$, $R_3$, and X in the general formula I can be produced.

It is difficult to purify the cyanine dye thus prepared by ordinary operations, such as distillation and recrystallization, so the dye is purified by extraction, e.g., the cyanine dye from which insoluble matter in chloroform has been removed is generally used, although a small amount of impurities may be contained in the dye. Although the chemical nature of the impurities has not been confirmed, the impurities may be those having only one cyanine structure due to the incomplete of reaction and having an acid moiety at the unreacted 2-methylene indoline moiety.

The dimer cyanine dye having a carbazole nucleus thus obtained shows an effective sensitizing effect for various organic photoconductors.

The amount of the dimer cyanine dye can be about 0.01 to about 10% by weight, based on the organic photoconductor weight. The most preferred range is from 0.1 to 0.5% by weight, based on the organic photoconductor weight. The dye is usually dissolved in a solvent and then mixed with the organic photoconductor.

The organic photoconductors to which the sensitizer of this invention is added can be treated by an ordinary electrophotographic method, e.g., the photoconductors described in U.S. Pat. Nos. 2,221,776; 2,297,691; 2,907,674; 3,081,263; 3,241,998; 3,189,447 (1,3,4-oxadiazole); 3,112,197 (1,3,4-triazole); 3,097,095 (imidazoline); 3,180,729 (pyrazoline); 3,037,861 (polyvinyl carbazole); 3,180,730 (triphenylamine); 3,162,532 (aromatic vinyl polymers), and the like. It is to be specifically noted that the organic photoconductors with which the present invention find particular application are not especially limited, but can be freely chosen from appropriate organic photoconductors as are known in the art.

One especially preferred organic photoconductor is poly-N-vinyl carbazole, preferably having a molecular weight of from about 5,000 to about 500,000.

The invention will described in more detail by the following examples, but the invention shall not be limited thereto.

## EXAMPLE 1

A solution prepared by dissolving 20 g of poly-N-vinyl-carbazole having a molecular weight of 300,000 and 50 mg of the dye prepared in Synthesis I in 200 ml of methylene chloride was coated in a dry thickness of about 10 microns on a paper which had been subjected to a conductive treatment (polyvinyl benzyl trimethyl ammonium chloride was coated in an amount of 2–4 g/m$^2$ on the paper).

The photosensitive material thus obtained was statically charged in the dark by an ordinary electrophotographic process (corona discharge) and then imagewise exposed to white light in an exposure amount of 31 lux-second. When the photosensitive material thus exposed was developed by an electrophotograhic developer or a toner prepared by adsorbing a 5:5 weight parts kneaded mixture of carbon black and polystyrene on glass beads 0.5 mm in diameter, a sharp image was reproduced. The results of testing the relationship of the proper exposure amount and the amount of the sensitizer are shown in the following table.

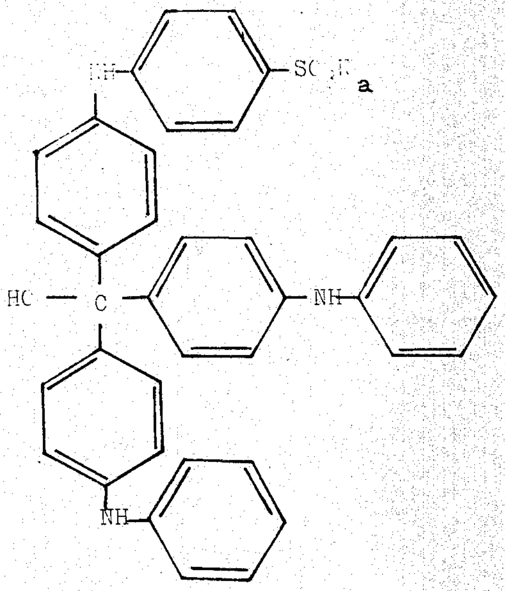
| Amount (mg) of sensitizer per 20 g of poly-N-vinyl carbazole | Proper exposure amount (lux-second) |
|---|---|
| none | 20,000 |
| 10 | 500 |
| 50 | 31 |
| 100 | 21 |
| 200 | 20 |
| 400 | 32 |

From the above results, it was confirmed that by the addition of the sensitizer the proper exposure amount was reduced and the sensitivity of the photosensitive material increased.

## EXAMPLE 2

The dye obtained in Synthesis II was added to 20 g of poly-N-vinylcarbazole and the sensitization effect was determined by the method of Example 1, the results of which are shown in the following table. As the electrophotographic developer, a dispersion of 1 g of a commercially available black offset ink in 1 liter of cyclohexane was used.

Composition of the ink
carbon black, 25 parts by weight;
alkali blue toner, 7 parts by weight;



rosin modified phenol-formaldehyde resin, 55 parts by weight;
boiled linseed oil, 13 parts by weight.

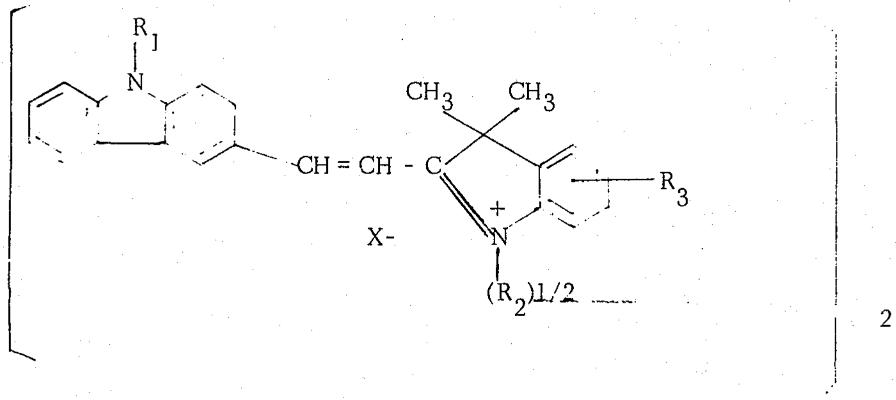
| Amount (mg) of sensitizer per 20 g of poly-N-vinyl carbazole | Proper exposure amount (lux-second) |
|---|---|
| none | 20,000 |
| 10 | 110 |
| 50 | 51 |
| 100 | 49 |
| 200 | 70 |
| 400 | 86 |

From the above results it was confirmed that by the addition of the sensitizer, the amount of exposure required was reduced and the sensitivity of the photosensitive material increased.

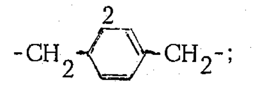
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What we claim is:

**1.** An electrophotographic photosensitive material comprising an organic photoconductor sensitized by a dimerized cyanine dye having a carbazole nucleus represented by the general formula

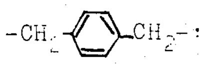


wherein $R_1$ represents a hydrogen atom; an alkyl group having 1–5 carbon atoms; an alkyl group substituted by a halogen atom, a hydroxyl group, or a cyano group; or an acyl group substituted by a halogen atom, a hydroxyl group, or a cyano group; $R_2$ represents $-(CH_2)_n-$ where *n* is a positive integer of 2 to 6 or



$R_3$ represents a hydrogen atom, a halogen atom, a nitro group, an alkyl group, —OR', or —COOR', wherein R' is an alkyl group having 1–5 carbon atoms; and X represents an anion residue.

**2.** The material as claimed in claim **1** wherein X is Cl, Br, I, $BF_4$, $ClO_4$ or



**3.** The sensitizer as claimed in claim **1** wherein said acyl group is selected from those of the formula $R_4CO$—, where $R_4$ is a $C_1$–$C_3$ alkyl group, benzyl or toluyl.

**4.** The sensitizer for an electrophotographic photosensitive material as set forth in claim **1** in which said electrophotographic photosensitive material contains an organic photoconductor.

**5.** The material for an electrophotographic photosensitive material as set forth in claim **4** in which said organic photoconductor is poly-N-vinylcarbazole.

**6.** The electrophotographic photosensitive material as set forth in claim **5** in which the amount of the dimerized cyanine dye is from about 0.01 to about 10% by weight of the organic photoconductor.

* * * * *